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OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract N00014-81-K-0526

R&T Code 413D003

# Solid Electrolytes for Multivalent Cations

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30 June 1990

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 413D003
Contract/Grant Number: N00014-81-K-0526
Contract /Grant Title: Solid Electrolytes for Multivalent Cations
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a. Number of papers submitted to refereed journals, but not published: 14
b. * Number of papers published in refereed journals **(for each, provide a complete citation):** 27
c. Number of books or chapters submitted, but not yet published: 1
d. * Number of books or chapters published **(for each, provide a complete citation):** 6
e. * Number of printed technical reports/non-refereed papers **(for each, provide a complete citation):** 2
f. Number of patents filed: 0
g. * Number of patents granted **(for each, provide a complete citation):** 0
h. * Number of invited presentations **(for each, provide a complete citation):** ____
i. * Number of submitted presentations **(for each, provide a complete citation):** 0
j. * Honors/Awards/Prizes for contract/grant employees (list attached): 0
k. Total number of **Full-time equivalent** Graduate Students and Post Doctoral associates supported during this period, under this R&T project number:
   Graduate Students: 4
   Post-Doctoral Associates: 1
  including the number of,
   Female Graduate Students: 1
   Female Post Doctoral Associates: 0
  the number of
   Minority* Graduate Students: 0
   Minority* Post Doctoral Associates: 0
  and, the number of
   Asian Graduate Students: 0
   Asian Post Doctoral Associates: 0
l. * Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

* Use the letter and an appropriate title as a heading for your list, e.g.:
  b. Published Papers in Refereed Journals, or, d. Books and Chapeters published
  Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disk

*Minorities include Blacks, Aleuts, Amindians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

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## a. Papers Submitted to Refereed Journals

K. Edstrom, J.O. Thomas, and G.C. Farrington,"A Single-Crystal X-ray Diffraction Study of the $Na^+/Cd^{2+}$ Ion Exchange Process in $Na^+$ ß-Alumina," Acta Cryst. (B)

J.O. Thomas and M.A. Zendejas,"MD Simulation as a Complement to Diffraction in the Study of Disordered Systems,", J. Computer-Aided Molecular Design, (submitted).

K. Edstrom, J. O. Thomas and G. C. Farrington, "Sodium Ion Distribution in $Na^+$ ß-Alumina: a Definitive X-ray Diffraction Study", Submitted to Acta Cryst. (B).

K. Edstrom, J. O. Thomas and G. C. Farrington, "Structural Aspects of the $Na^+$ to $Cd^{2+}$ Ion Exchange Process in $Na^+$ ß-Alumina", Submitted to Acta Cryst. (B)

K. Edstrom, J. O. Thomas and G. C. Farrington, "A Single-Crystal Diffraction Study of the Ion Exchange of $Cd^{2+}$ into $Ag^+$ ß-Alumina", Submitted to Acta Cryst. (B)

K. Edstrom, W. Carrillo-Cabrera, J. O. Thomas and G. C. Farrington, "Structural Evidence of Water Uptake in $Na^+$ ß-Alumina", Submitted to Solid State Ionics.

G. S. Rohrer, J. O. Thomas and G. C. Farrington, "The Structure and Properties of Sn(II) ß"-Alumina", Chem. of Materials (in press)

J. O. Thomas, L. Momoda, B. Dunn and G. C. Farrington, "The Relationship between Structure and Optical Properties in the Mixed-Ion System $Na^+/Ce^{3+}/Nd^{3+}$ ß"-Alumina, Solid State Ionics (in press)

M. A. Zendejas and J. O. Thomas, "Conductions Mechanisms in Solid Electrolytes: $Na^+$ ß-Alumina", Physica Scripta (in press)

C. Lane, G. C. Farrington, J. O. Thomas, and M. A. Zendejas, "Molecular Dynamics Simulation of Ion Transport in $Na^+/Ba^{2+}$ ß"-Alumina", Solid State Ionics (in press)

J.D. Barrie, L.A. Momoda, B. Dunn, D. Gourier, G. Aka and D. Vivien, ESR and Optical Spectroscopy of Ce3+ ß" Alumina, Journal of Solid State Chemistry (Other support: Franco-American Commission)

K.K. Shin, J.D. Barrie, B. Dunn and J.I. Zink, Optical Spectroscopy of $Cu^{+}/Ag^{+}$ ß″-Alumina, Journal of the Americal Chemical Society (Other support: NSF)

G. Aka, B. Dunn, J. Foreman and G.C. Farrington, Crystal Growth and Transport Properties of Sodium ß and Sodium ß″-Aluminogallates, Solid State Ionics.

J.O. Thomas, L.A. Momoda, B. Dunn and G.C. Farrington, The Relationship between Structure and Optical Properties in the Mixed-Ion System $Na^{+}/Ce^{3+}/Nd^{3+}$ ß″-Alumina, Solid State Ionics (Other support: Swedish Research Council)

**b. Papers Published in Refereed Journals**

B"-Alumina: A Solid Electrolyte as a Solid State Laser Host. B. Dunn, J.O. Thomas & G.C. Farrington. In: "Spectroscopy of Laser-Like Materials". Ed: B. DiBartolo. 1988. Plenum Press, New York.

The Effect of Quenching on the $Na^{+}$ Ion Distribution in $Na^{+}$ B"-Alumina. M. Alden, J.O. Thomas. & P. Davies. Solid State Ionics, 18.19, 694-698 (1986).

The $Eu^{3+}$ $Eu^{2+}$ Reduction Process in $Eu^{3+}$ B"-Alumina. W. Carrillo-Cabrera, J.O. Thomas & K.G. Farrington. Solid State Ionics. 18/19, 645-652 (1986).

The Hydration of Selected Divalent B"-Aluminas. Rohrer, G.S., Thomas, J.O. & Farrington, G.C. Chemistry of Materials, 3 (1991) 325-332.

A Single-Crystal X-ray Diffraction Study of the Ion Exchange of $Cd^{2=}$ into $Ag^{+}$BAlumina. Edstrom, K., Thomas, J.O. & Farrington, G.C. Acta Cryst. B47 (1991) 643.

The Sodium Ion Distribution in $Na^{+}$ B-Alumina: A Challenge to Crystallography. Edstrom, K., Thomas, J.O. & Farrington, G.C. Acta Cryst. B47 (1991) 105-109.

Structural Aspects of Water uptake in $Na^{+}$B-Alumina. Edstrom, K., Carrillo-Cabrera, W., Thomas, J.O. & Farrington, G.C. Solid State Ionics 47 (1991) 105-109).

M.A. Saltzberg, J.O. Thomas, and R. Wappling,"Mossbauer Spectroscopy Studies of the Reduction of Eu(III) in Beta" Alumina," Solid State Ionics, 28-30, 1563 (1988)

J.O. Thomas, and G.C. Farrington,"Structural Evidence for the Interstitialcy Mechanism in Beta Alumina," K. Edstrom, Solid State Ionics, 28-30, 363 (1988)

M.A. Zendejas and J.O. Thomas,"A Molecular Dynamics Simulation Study of Long-Range Ionic Distributions in $Na^+$ ß"-Alumina," Solid State Ionics, 28-30, 46 (1988)

W. Carrillo-Cabrera, J.O. Thomas, and G.C. Farrington, "The Structures of the Lanthanide Gd(III), Eu(III), and Nd(III) Beta" Aluminas," Solid State Ionics, 28-30, 317 (1988)

J.O. Thomas, and P.E.D. Morgan, "Preparation and Structure of Li-Stabilized $Na^+$ Beta" Alumina Single Crystals," B. Dunn, B.B. Schwarz, Solid State Ionics, 28-30, 301 (1988)

G.S. Rohrer and G.C. Farrington, "Electronic Conductivity in Pb(II) Beta" Alumina,"Solid State Ionics, 28-30, 1142 (1988)

G.S. Rohrer, P.K. Davies, and G.C. Farrington, "The Effect of Thermal History on the Ionic Conductivity of Pb(II) Beta" Alumina,"Solid State Ionics, 28-30, 354 (1988)

M.A. Saltzberg, F.R. Garzon, P.K. Davies, and G.C. Farrington, "Properties and Microstructures of a Mixed Valency Solid Electrolyte: Na(I)-Eu(II) Beta" Alumina," Solid State Ionics, 28-30, 386 (1988)

M. A. Saltzberg, J. O. Thomas and G. C. Farrington,Short- and Long-Range Order in Na(I)-Eu(II) β"-Alumina, Chemistry of Materials 1, 19 (1989)

Letters from Iceland II: Report from the Workshop on Future Trends in Solid State Ionics, II: Discussion Groups on Crystalline Electrolytes and Non-Crystalline Electrolytes, Eds. J. O. Thomas and G. C. Farrington, Solid State Ionics, 31, 159 (1988)

J.D. Barrie, B. Dunn, O.M. Stafsudd, M.A. Saltzberg, R. Seshadri, and G.C. Farrington,"Structure/Optical Property Relationship in Multiple Ion Exchanged ß"-Aluminas," Solid State Ionics, 28-30, 344 (1988)

G. S. Rohrer and G. C. Farrington,"Defect Formation in Ag(I)-, Pb(II)-, Sn(II)-, and Bi(III)-ß"-Aluminas," Chemistry of Materials 1, 438 (1989)

B. Dunn, G.C. Farrington, and J.O. Thomas,"New Frontiers in Beta" Alumina Research," Materials Research Bulletin 14, 22 (1989)

J. O. Thomas and M. A. Zendejas, "Molecular Dynamics Simulation as a Complement to Diffraction in the Study of Disorder in Crystals", J. of Comp.-Aided Mol. Design, 3, 311 (1989)

B. Dunn, G. C. Farrington, and J. O. Thomas, "Frontiers in ß"-Alumina Research", MRS Bulletin (Review), XIV(9), 22 (1989)

M. A. Saltzberg and G. C. Farrington, "Eu-O Bonding and Spectroscopy of Eu(III) in ß"-Alumina," J. Solid State Chem. 83, 272 (1989)

B. Dunn, G. C. Farrington and J. O. Thomas, "Imaginary Structures and Guided Light Beams," ISSSI-Bulletin

L.A. Momoda, J.D. Barrie and B. Dunn, The Use of Multiple Ion Exchange to Produce Energy Transfer in ß" Alumina, Materials Research Bulletin 24, 859 (1989)

B. Dunn, G.C. Farrington and J.O. Thomas, Frontiers in ß" Alumina Research, Materials Research Society Bulletin 14, 22 (1989) (Other support: NSF and Swedish Research Council)

R. Twardowski, M. Eyal, R. Reisfeld, L.A. Momoda and B. Dunn, *Energy Migration and Energy Transfer in the System Ce(III)/Tb(III) in* ß"-Alumina Crystals, Chemical Physics Letters 168, 211 (1990) (Other support: Enrique Berman Fund)

## c. Books (and sections) Submitted for Publication

G. C. Farrington, B. Dunn, and J. O. Thomas,"The Multivalent Beta" Aluminas", Advances in Solid State Ionics, T. Takahashi, ed. (in press)

## d. Books (and sections) Published

G. C. Farrington, B. Dunn and J. O. Thomas,"The Multivalent ß"-Aluminas," Intl. Seminar on Solid State Ionic Devices, 18-23 July, 1988, Singapore, p. 105, World Scientific Publ. Co., Singapore

G. C. Farrington, B. Dunn and J. O. Thomas, "The Multivalent $\beta$"-Aluminas", Invited chapter in: "High Conductivity Solid State Ionics Conductors", Editor: Takahashi, T. World Sci. Publ. Co., Singapore 1989

G. C. Farrington, B. Dunn and J. O. Thomas, "The Multivalent $\beta$"-Aluminas", Invited chapter in: "High Conductivity Solid State Ionics Conductors", Proceedings of the Asian Conf. on Solid State Ionics, Editor: Takahashi, T. World Sci. Publ. Co., Singapore 1989

G.C. Farrington, B. Dunn and J.O. Thomas, "The Multivalent ß" Aluminas," in High Conductivity Solid Ionic Conductors: Recent Trends and Applications, T. Takahashi, ed. (World Scientific, Singapore, 1989) pp. 327-365 (Other support: NSF and Swedish Research Council)

L.A. Momoda, J.D. Barrie, B. Dunn and O.M. Stafsudd, "Energy Transfer Effects in ß" Alumina," in Excited States of Transition Elements, B. Jezowska-Trzebiatowska, J. Legendziewicz and W. Strek, eds. (World Scientific, Singapore, 1989) pp. 368-384.

J.D. Barrie, B. Dunn and O.M. Stafsudd, "Effect of Heteroatomic $d_{10}$ Interactions on the Optical Properties of Cu+ Doped Ag+-ß" Alumina," in Optical Materials Processing and Science, D.B. Poder and C.Ortiz, eds., Materials Research Society Symposium Vol.152 (Materials Research Society, Pittsburgh, 1989) pp. 89-94

**e. Technical Reports Published and Papers Published in Non-Refereed Journals**

K. Edstrom, "Diffraction as a Tool in the Study of Mechanisms for Ionic Conductivity in Solids", Acta Univ. Upsaliensis (Thesis. Univ. of Uppsala, Sweden), 1990

S.C. Adams, Refractive Index Tuning in ß" Alumina and Optical Device Applications, Ph.D. Dissertation, University of California-Los Angeles, November, 1989

**f. Patents Filed**

**g. Patents Granted**

**h. Invited presentations**

**i. Contributed presentations**

**j. Honors/Awards/Prizes for contract/grant employees**

**k. Full-time equivalent Graduate Students and Post Doctoral associates**

Students:
Penn - J. Foreman and C. Lane
Uppsala - K. Edstrom and Å. Wendsjo

Post-doc:
Uppsala - M. Zendejas

**Brief Description of Project**

The ß and ß″ aluminas are well appreciated as a unique family of materials with remarkable structural, transport and optical properties. Their rich ion exchange chemistry makes it possible to chemically 'tune' the mobile ion composition so that specific properties are developed within the ß″ alumina framework. As ionic conductors, the ß″ aluminas are the first solids to exhibit high conductivity for divalent and trivalent cations, while the transition-metal and lanthanide-containing ß″ aluminas exhibit some exceptional optical properties. The present research program builds upon the structure/property relationships that we have established for the multivalent ß″ aluminas.

The overall objective of the research is to utilize the ß and ß″ alumina family of materials as a model system in which to design and synthesize compounds with pre-determined properties. This family of materials (which includes aluminates, ferrites and gallates) is unique because a single structure type is maintained as one alters not only the chemical nature of the mobile ions but also the chemical nature of the framework. The program involves interrelated activities including crystal growth, chemical synthesis and studies of structure, ion transport, hydration and optical properties. An important focus of the project is to closely couple model experiments on structure, ion transport and optical behavior with molecular dynamics (MD) simulations.

**b. Significant Results**

This program has carried out wide-ranging studies of the preparation, chemical properties, electrochemical and optical characteristics, and structural aspects of the multivalent beta" aluminas, the first family of solid electrolytes

in which divalent and trivalent cations are mobile. Potential applications of these materials that have been explored are in solid state lasers, phosphors, sensors, and batteries.

Some of the most intriguing results of this work have come from molecular dynamics simulations of the structure and dynamics of ion motion in both ß and ß" alumina. Simulations of the sodium containing forms as well as mixed sodium-cadmium ß" alumina have provided profound insight into the mechanisms by which ions move in the structures on the unit cell level. Simulations have focused on understanding the influence of interstitial oxygen ions on conductivity in sodium ß alumina. These have clearly shown that the interstitial oxygen ions can serve as local traps for mobile sodium ions and that the introduction of divalent cations to the structure releases sodium ions from these traps and increases the effective charge carrier concentration in the structure. Simulations of sodium ß" alumina have begun to reveal the influence of magnesium ions in the structure on ion arrangement and conductivity in the conduction planes and also have shown how local ion-vacancy ordering leads to conduction planes which are actually dynamic mosaics of ion motion and immobility. Finally, simulations of mixed sodium-barium ß" alumina have 'predicted' with remarkable accuracy the variation of ion transport observed experimentally as a function of composition. The simulations, however, provide detailed insight into the local structures responsible for the variations.

Taken together, these simulation studies have advanced considerably our understanding of this particular set of compounds as well as the techniques used to simulate and predict the characteristics of ion motion in solid electrolytes in general. The original goals of this work were to use simulation to predict the properties of experimentally unknown compositions, and progress towards this goal, at least in one small set of real and hypothetical materials, has been considerable indeed.

In addition, another fascinating study has been completed of the refractive index of ion exchanged ß″ aluminas. The unique ability to change the composition of the compound without changing its structure type has made it possible to compare experimental results with calculations derived from theoretical treatments. Measurements of the ordinary and extraordinary refractive indices were readily fit to the Clausius-Mossotti relation which is based on highly ionic compounds. These results confirm that cation-oxygen bonds for conduction plane ions are extremely ionic; with the c-direction exhibiting greater ionicity than within the ab plane. Similar conclusions were reached in the spectroscopy of Eu(III) ß″ alumina. In related work on ß-alumina, a mixed Na(I)-Ag(I) composition was able to attain an iso-index point for wavelengths in the visible.

Spectroscopy studies of infrared emitting ions Ho(III) and Er(III) were completed and their prospects as laser materials were evaluated. Both ions exhibited extremely strong hypersensitive transitions. This characteristic of the ß″ alumina structure arises from the ability of lanthanide ions to be slightly displaced from their equilibrium positions in the conduction plane.

Stimulated emission cross sections for Ho (at 2.1 μm) and Er (at 1.6μm) gave values comparable to those for typical laser hosts and indicates that laser oscillation can be produced for these ions in the ß″ alumina host lattice. The high quantum efficiency (≈100%) for Er(III) is particularly attractive for laser action.

Research on the synthesis and properties of ß and ß″ aluminogallates emphasized studies of the defect chemistry of the grown single crystals of the sodium compounds. The non-stoichiometry in the ß″ aluminogallates was attributed to Mg(II) substitution for Al(III) in the spinel block. The composition corresponds to the formula $Na_{1+x}Al_x(Al_{1-y}Ga_y)_{11-y}O_{17}$ with x in the range of 0.67. The defect chemistry of the ß-aluminogallates is less clearly established. The excess sodium content is initially in the range of 0.7, however, simple chemical washing in $NaNO_3$ lowers this value to 0.3. The origin of this behavior and its effect on conductivity are being investigated. NMR results have shown that Ga(III) substitutes preferentially for Al(III) in tetrahedral sites in the spinel block.